

The Structural Interpretation of DSC Curve Specificity of Poly(caprolactam) Fibers. I. The Specificity of the Element of the Curve Observed in the Temperature Range $\sim 40\text{--}65^\circ\text{C}$

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Synopsis

The index τ determined from the thermogram was correlated with the selected parameters of the amorphous material structure of polycaprolactam fibers. The investigated structural parameters were as follows: (a) the orientation factor determined by infrared absorption spectroscopy, based on the absorption band at 1130 cm^{-1} ; (b) the fraction of taut tie molecules calculated on the basis of the determined axial elastic modulus and volume crystallinity of the fiber. The occurrence of straight-line relations between the values of the index τ and the values of the investigated structural parameters was found out. The conclusion was formulated that the specificity of the investigated element of the DSC curve reflects the entropy transition rate. That transition, stimulated by fiber heating during the DSC experiment, consists of the increase of the disorder of taut tie molecules. Probably, the rate of that transition changes relatively to the magnitude of the stress affecting taut tie molecules.

INTRODUCTION

Thermal analysis is the technique which has actually been quite extensively applied for polymer investigations.¹ Frequently, experiments of this type are carried out using differential scanning calorimetry (DSC). It results from the fact that the DSC method allows the possibility of a relatively quick and precise determination not only of the temperature range, but also the heat of a given transition. As is known, determinations of this type may constitute the base for, among others, characterizing supermolecular polymer structure. Polymer crystallinity evaluation, based on the heat of fusion measurement may be given as an example.² Unfortunately, the above example is quite isolated. Other important parameters of polymer structure are not determined by the DSC method as a rule. Presumably, this state of affairs results mainly from the fact that the appropriate relations are not known. Those are the relations which would connect the DSC image corresponding to a given transition, with the structural specificity of those polymer regions within the range of which the transition would be realized.

It seems that revealing the relations between the specificity of the DSC curve and the amorphous regions structure of semicrystalline polymer in the fiber form would be particularly interesting both from the theoretical and practical points of view. Taking the above into consideration, an endeavor has been made in this study to show, on the example of polycaprolactam fibers, if such relations really exist. Maybe indicating that problem will contribute both a more extensive

application and the DSC method and better knowledge of the internal polymer structure.

THE CHARACTERISTIC OF THE INVESTIGATED DSC CURVE ELEMENT

The thermogram of polycaprolactam fibers, typical for the temperature range 25–150°C is shown in Figure 1. The presented fragment of the DSC curve comprises two basic elements. One of them being a large endothermic peak ABC. The second element marked as DEF was the main object of interest in this study. Specifically, the parameter regarded as characterizing the specificity of that DSC curve element was correlated with the definite parameters of the amorphous material structure of the fibers investigated.

It should be pointed out that when discussing the DEF element of the DSC curve, this particular element of polycaprolactam fibers thermogram is to be found only when the specific conditions of the DSC investigation are maintained. It is essential to give the fibers from which the specimen for DSC investigation was prepared suitably long relaxation time (irrespective of whether the sample is prepared from the fibers rolled ball-like or powdered on the microtome). The DEF element is not be found on the thermogram obtained using the specimen prepared directly before the DSC measurement. It appears slightly shaped only when the specimen was prepared at least 2 days before the experiment, whereas the fibers which relaxed in the form of specimen for 4–5 days, give a very clear shape of DEF element of the DSC curve. Starting from the first week of fibers relaxation, the specificity of the DSC curve element investigated is not practically changed.

THE CHARACTERISTICS OF THE PARAMETERS WHICH WERE CORRELATED

In order to characterize the specificity of the investigated DSC curve element,

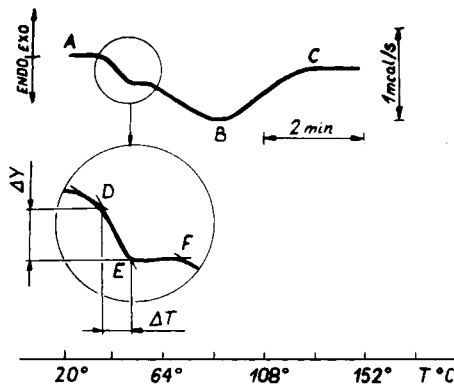


Fig. 1. DSC thermogram fragment of polycaprolactam fibers, typical for the temperature range 20–150°C.

the index τ , defined as follows, was used:

$$\tau = \frac{\Delta T \cdot m}{\Delta Y} \left(\frac{\text{s}}{\text{J/K} \cdot \text{g}} \right) \quad (1)$$

where ΔT (K) and ΔY (J/s) are the parameters of the DSC curve element investigated, determined from the thermogram (see Fig. 1) and m = the mass of the sample (g).

It was found out that the value of the index τ , obtained for a given sample under various conditions of the DSC investigation is not dependent on any apparatus parameters of the experiment, except for the heating rate. It appeared that values of the τ dependence on the heating rate (HR) properly describe the following general equation:

$$\tau = b \cdot (\text{HR})^a \quad (2)$$

where a = constant value for the investigated polycaprolactam fibers and b = constant value for a given sample.

Constant values a and b can be determined for a given sample from the diagram of the straight line described by the equation [eq. (2) rearranged]:

$$\log \tau = a \log (\text{HR}) + \log b \quad (3)$$

The constant a value determined from many diagrams of such straight lines—obtained for a large number of different samples—was practically the same: $a = -0.477$.

The constant b value determined from any diagram of the straightline described by eq. (3) is (for $\log \text{HR} = 0$, i.e., for $\text{HR} = 1$):

$$b = \tau_{\text{HR}=1} \quad (4)$$

After substitution of (4) into (2) and conversion, we obtain

$$\tau_{\text{HR}=1} = \tau / (\text{HR})^a \quad (5)$$

The value $\tau_{\text{HR}=1}$ calculated from formula (5) is constant for a given sample, irrespective of the heating rate. Considering the above, the discussed value has been named the corrected value of the index τ .

The corrected values of the index τ were correlated with the values of the selected parameters of the amorphous material structure of the investigated polycaprolactam fibers. The parameters which point out the specific fiber features were selected, distinguishing that fiber among other polymer products. As axial orientation and fibrillar structure of the fiber were regarded as such features, two parameters were selected: f_a , the orientation factor of the amorphous region, and β , the fraction of tie molecules in the amorphous layer.

The orientation factor f_a was determined using infrared absorption spectroscopy. The individual values were calculated from the following formula, based on the equation derived by Fraser³ and on Hermans' definition of the orientation factor⁴:

$$f_a = \frac{R - 1}{R + 2} \frac{2}{3 \cos^2 \alpha - 1} \quad (6)$$

where R = the dichroic ratio and α = the angle of transition moment of the respective absorption band.

The fraction of tie molecules was determined according to the assumptions of Peterlin fibrillar model of fibrous structure.^{5,6} According to this, the value β , given as the volume fraction of taut tie molecules (TTM) in the amorphous layer, was calculated as follows⁷:

$$\beta \cong \frac{E(1 - v_c)}{E_c - E \cdot v_c} \quad (7)$$

where E_c , E = the axial elastic moduli of the crystalline region and fiber, respectively, and v_c = the volume crystallinity of the fiber.

EXPERIMENTAL

The object of investigations were polycaprolactam fibers manufactured in Poland. There were five fiber samples in the first series, of differentiated draw ratio in the range 150–350%, every 50%. The second series also consisted of five samples. In that case, each sample comprised the fibers with draw ratio 250% annealed unstressed in the dryer for 2 h, at temperature T_A , in air. Individual temperatures were the following: $T_A = 100, 120, 140, 160, 180^\circ\text{C}$. After annealing, the fibers were kept in the closed dryer for 24 h, until completely cooled down to room temperature.

The samples were prepared for DSC investigation by rolling the fibers between fingers to form the ball of mass $m = 3.00\text{--}4.00$ mg. The fibers in this form closed in the DSC pan constituted a single specimen. The specimens were kept at the room temperature for 1 week and under relative humidity conditions $\sim 60\%$. After that period of relaxation the fibers were ready for DSC investigation.

DSC thermograms, forming the base for the determination of the index τ values were made using a DuPont 990 Thermal Analyser. The conditions of measurements were the following: atmosphere = air, heating rate = 20 deg/min, Y = axis range, 1 mcal/s-in., time base setting = 2 in./min.

Infrared absorption spectra used for the orientation factor f_a were made using a Specord IR-71 Double-Beam Spectrometer, equipped with a selenium polarizer. The absorption band at 1130 cm^{-1} corresponding to —C—C— vibrations was taken as the base for determination.⁸ The value of the angle of transition moment, indispensable for calculation of f_{a1130} was assumed to be $\alpha = 31^\circ 10'$.⁹

The investigations of the axial elastic moduli of the fibers were carried out using an Instron Testing Instrument, applying the crossheadspeed 2 cm/min. The value $E_c = 240$ (GPa) was assumed for calculations.¹⁰

The volume crystallinity of the fiber was calculated from the well-known formula:

$$v_c = \frac{d}{d_c} w_c \quad (8)$$

where d = the density of the fiber, d_c = the effective density of the crystalline region, and w_c = the weight fraction crystallinity of the fiber. (Those values were determined using wide-angle X-ray diffraction. Details concerning these investigations will be given in the second part of the study to be submitted for printing.)

The density d was measured at the temperature 25°C using flotation technique, in carbon tetrachloride- n -heptane mixture. The effective density was calculated for each sample separately, based on determining, for that particular sample, the relative amounts of the crystalline component in the α and γ forms. (Those values were determined using wide-angle X-ray diffraction. Details concerning these investigations will be given in the second part of the study to be submitted for printing.) The effective density was used for calculation of v_c , in place of the ideal density routinely used for this purpose.

RESULTS AND DISCUSSION

The results of experiments are given in Table I, whereas the relations occurring between the corrected index τ values and the values of the investigated parameters of fiber structure are presented as diagrams in Figures 2 and 3.

Basing on the preliminary observation of the straight line character of the diagrams presented in Figures 2 and 3, the following general conclusion may be given: The specificity of the investigated element of the DSC curve remains in close relation to the structure of the amorphous regions in the fiber investigated. Therefore, it may be particularly stated that the specificity of the investigated element of the DSC curve is determined by orientation of the amorphous material and the fraction of TTM. It should be mentioned with respect to orientation that the relations to be found between factor f_{a1130} and parameter β are of the same straight-line character as the relations occurring between the corrected index τ values and the values of β . Therefore, it may be assumed that factors f_{a1130} is not characteristic for the orientation of the whole amorphous material, but only describes the orientation of TTM. It seems quite probable. On the one hand, the possibility of rather exceptional situating of TTM as "taut" elements of the fibrillar fiber structure may not be excluded. On the other hand, however, there should be considered the fact that the absorption band at 1130 cm^{-1} corresponds to the vibrations of the element situated along the macromolecular axis. It seems likely in this approach that the diagrams presented

TABLE I
Values of Index τ and Determined Parameters

Sample	Index τ (corrected values) (ks/J/K-g)	Orientation factor f_{a1130}	Volume Crystallinity v_c	Axial elastic modulus E (GPa)	Fraction of TTM $\beta \times 10^{-2}$
Draw ratio (%)					
150	4.908	0.649	0.24	3.40	1.08
200	3.552	0.475	0.24	4.21	1.34
250	3.389	0.457	0.24	4.35	1.38
300	3.121	0.424	0.24	4.56	1.45
350	2.963	0.400	0.24	4.64	1.48
Annealing temp (°C)					
100	3.623	0.674	0.55	4.43	0.84
120	4.095	0.769	0.58	4.66	0.83
140	4.308	0.810	0.56	4.42	0.82
160	5.114	0.972	0.58	4.48	0.79
180	5.272	0.985	0.59	4.52	0.78

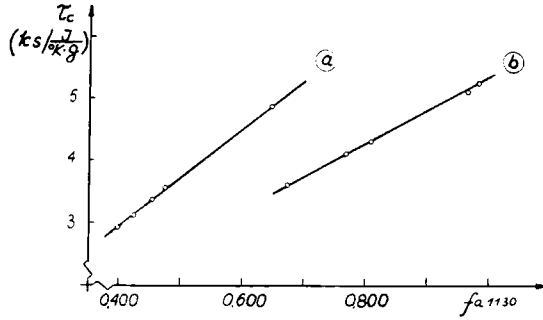


Fig. 2. The index τ as a function of the orientation factor: (a) the annealed fibers; (b) fibers of a differentiated draw ratio.

in Figure 2 show the changes in the specificity of the investigated element of the DSC curve, relatively to the changes in the orientation of TTM.

Before analyzing those changes which are presented in Figures 2 and 3, the sense of the index τ should be first interpreted. From the formal point of view, only the conventional meaning of units, by which the index τ is expressed, could be the base for such an interpretation. According to this approach, the index τ may be defined as the time during which the specific heat of the material DSC investigated changes by 1 unit (i.e., $1 J/^\circ K \cdot g$). However, it should be noted, when realizing the structural interpretation, that the complex of units as a whole, $J/K \cdot g$, constitutes not only the specific heat unit, but also the specific entropy unit. The above fact seems to be worth pointing out in the context of searching for the reason of the change of the specific heat. It seems that the specificity of defined transition, occurring within the amorphous material of the investigated fiber, may be regarded as that reason. This transition is recorded on the thermogram in the shape of the DEF element of the DSC curve. It is known, from another source, that the DSC image of this type is characteristic of the so-called entropy transition. It may be assumed that the specificity of a given entropy transition will be reflected in the specificity of the DSC image of that transition. Therefore, the index τ defining the specificity of the investigated element of the DSC curve

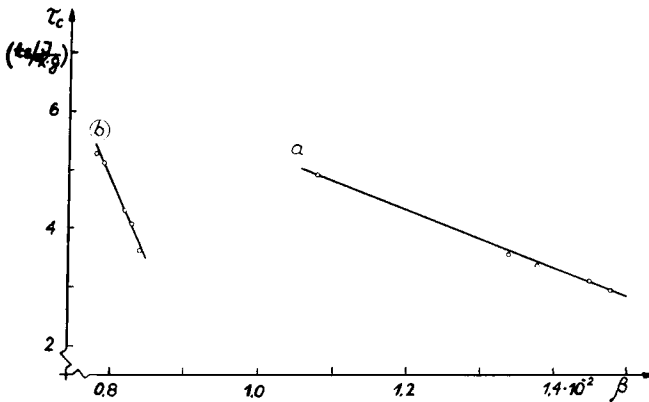


Fig. 3. The index τ as a function of the fraction of TTM.

could also characterize the specificity of a given entropy transition. Assuming the above and considering the sense of units mentioned earlier, it seems that the index τ may be interpreted as the time during which the specific entropy of the material investigated changes by 1 unit (i.e., 1 J/K-g). In order to specify this definition, the sense of the relations shown in Figures 2 and 3 should be considered. In this context, the index τ may express the time of the change by 1 unit of the specific entropy of TTM. It is likely that it is this change of entropy which is connected with the change in the orientation of TTM. It may be assumed that the "change" specifies in this case the increase of entropy caused by the increase of the disorder of TTM. The increase of the disorder may directly result from the decrease of the orientation of TTM—which is the process occurring as a result of heating the sample during DSC measurement.

The analysis of diagrams in Figure 2 shows that the time τ increases with the increase of the orientation of TTM. That denotes, most generally, that the larger the degree of orientation of TTM, the more difficult it is to cause their disorientation. More strictly speaking, the larger the degree of the orientation of TTM, the slower the rate of the process thermally stimulated of their disorientation. Therefore, it may be supposed that the effect of a factor, which factor counteracts the disorientation of TTM, is intensified with the increase of the orientation. It seems that the stress acting on the individual tie molecules is that factor. The larger the degree of orientation, the larger will be the stress and, in consequence, the slower will be the disorientation process leading to the relaxation of the stress. The external illustration of the disorientation of TTM progressing at a slower rate will be recording of larger time τ value. The larger time τ values were recorded for the fibers of a differentiated draw ratio in comparison with the annealed fibers. This particular arrangement of results may testify, in the light of the presented discussion, that, in the case of annealed fibers, the TTM are less "taut" than for the drawn fibers. The above conclusion may be an additional proof for the generally recognized fact that fiber-annealing results in the internal stress-relaxation.

The analysis of the straight lines run in Figure 3 shows that the value of time τ decreases with the increase of the fraction of TTM. This character of relations may also be interpreted from the point of view of stress values acting on TTM. The larger the fraction of TTM, the smaller will be the true stress affecting the individual element. Consequently, the process rate of the disorientation of TTM will be higher. As a result, smaller values of time τ will be recorded. Displacement of the diagram for the annealed fibers towards smaller values β seems to prove the conclusion previously formulated, that in this case the TTM are less "taut" than for the fibers only drawn.

CONCLUSIONS

It may be stated to sum up that some relations exist between the specificity of the DSC curve and the structure of the investigated polycaprolactam fibers. Particularly, the entropy transition rate is reflected by the specificity of the investigated element of the DSC curve. The transition consists of the deterioration of the orientation of TTM, which is the process stimulated by heating the fiber during DSC investigation. It is likely that the rate of the transition is dependent on the magnitude of the stress affecting TTM. Slower transition (TTM more

stressed) is observed for the fibers only drawn, when compared to the annealed fibers.

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